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Sep 4, 1985

DERWENT-ACC-NO: 1985-258933

DERWENT-WEEK: 198542

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TITLE: Water-hardenable inorganic compsn. for tiles etc. - contains cement, gypsum, acrylate! polymer, water and water-reducing agent for high strength prod.

PATENT-ASSIGNEE:

ASSIGNEE

CODE

INOUE H

INOUI

PRIORITY-DATA: 1984JP-0028234 (February 16, 1984)

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PATENT-FAMILY:

PUB-NO

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LANGUAGE

PAGES

MAIN-IPC



JP 60171260 A

September 4, 1985

004

APPLICATION-DATA:

PUB-NO

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DESCRIPTOR

JP 60171260A

February 16, 1984

1984JP-0028234

INT-CL (IPC): C04B 22/00; C04B 24/26; C04B 28/00

ABSTRACTED-PUB-NO: JP 60171260A

BASIC-ABSTRACT:

The compsn. comprises 10-90 wt. pts. of water-hardenable cement e.g. portland cement, etc., 10-90 wt. pts. of water-hardenable gypsum e.g. alpha- or beta-CaSO₄.1/2H₂O, anhydrous CaSO₄ etc., 17-25 wt. pts. of H₂O (including amt. of H₂O contained in the acrylic water-dispersible organic polymer), 2-16 pts. wt. (calculated in terms of solids content) of acrylic water-dispersible organic polymer exhibiting water-reducing effect, e.g. methylmethacrylate- 2-ethylhexylacrylate copolymer, styrene-butylacrylate copolymer etc., and 0.5-2.0 pts. wt. of water-reducing agent e.g. Na salt of melamine sulphonate-formaldehyde condensate, etc.

USE/ADVANTAGE - The compsn. is suitable for use in prodn. of tile, block, roofing material, interior finishing material, floor material, ceiling material etc. Prods. exhibit high strength and excellent water resistance, incombustibility, weather-proofingness and vibration absorbability without generation of deformation, cracking, expansion and shrinkage.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: WATER HARDEN INORGANIC COMPOSITION TILE CONTAIN CEMENT GYPSUM
POLYACRYLATE POLYMER WATER WATER REDUCE AGENT HIGH STRENGTH PRODUCT

DERWENT-CLASS: A93 L02

CPI-CODES: A12-R01; L02-C05; L02-D07A;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1767U

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0004 0203 0044 0231 0306 3152 0486 0487 0495 3034 0502 3013 0530 0537
0565 1276 1278 1517 1737 1962 2012 2504 3251 2604 2605 2609 2615 2629 2679 3255
2691 2694 2696 2698 3275

Multipunch Codes: 014 034 038 04- 05- 051 055 056 06- 074 076 077 080 081 082 09-
139 14- 145 180 185 189 225 230 231 249 27& 397 436 53& 532 533 535 539 540 541 542
543 546 549 551 552 554 567 57& 58& 59& 613 614 616 618 623 626 681 688

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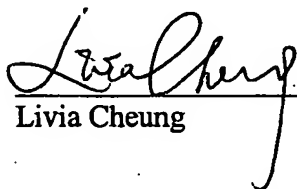


TRANSPERFECT
TRANSLATIONS

City of New York, State of New York, County of New York

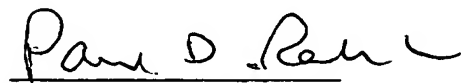
I, Livia Cheung, hereby certify that the following is, to the best of my knowledge
and belief, a true and accurate translation of this document, "Hydraulic Inorganic
Composition – S60-171260", from Japanese into English.

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Request for examination Not yet requested Number of inventions 1 (Total of 4 pages)

(54) Title of the invention	HYDRAULIC INORGANIC COMPOSITION	
	(21) Japanese Patent Application	S59-028234
	(22) Date of Application	16 February 1984
(72) Inventor	Inoue, Hiroyuki	263 Ota-ha, Ota-cho, Ota City
(71) Applicant	Inoue, Hiroyuki	263 Ota-ha, Ota-cho, Ota City

SPECIFICATION

1. TITLE OF THE INVENTION

Hydraulic inorganic composition

2. SCOPE OF PATENT CLAIMS

A hydraulic inorganic composition that is characterized in that it comprises,

- a) 10 - 90 parts by weight of a hydraulic cement,
- b) 10 - 90 parts by weight of a hydraulic gypsum,
- c) 17 - 25 parts by weight of water (including the moisture contained in the acryl water-dispersing organic polymer of d),
- d) 2 - 16 parts by weight of an acrylic, water-dispersing organic polymer that has a moisture-reducing effect (solid portion converted), and
- e) 0.5 - 2.0 parts by weight of a moisture-reducing agent.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a hydraulic inorganic composition that realizes water resistance and high strength without the occurrence of deformation or cracking and that permits thin, hardened bodies with large dimensions to be formed easily.

Conventionally, inorganic products that are manufactured of cement, gypsum, or clay or that are manufactured of a

compound in which an organic polymer or inorganic compound is combined with an inorganic composition already exist, but items manufactured of cement have the disadvantage that they are subject to low fracture toughness, low flex strength, occurrence of efflorescence, occurrence of constriction cracking, slow strength manifestation, etc. In addition, items manufactured of gypsum have the disadvantage that they have a low mechanical strength and are poor in water resistance and items manufactured of clay have the disadvantage that they must be fired at high temperatures to produce a high mechanical strength and that production yields are low as a result of deformation and cracking in the drying and firing stages. Moreover, inorganic products in which a water-dispersing organic polymer has been compounded with a cement - gypsum composition have been developed frequently in the prior art, but almost all of these have been poor in mechanical strength and water resistance, and the manufacture of those that have attained a fairly high strength (a flex strength of 200 kg/[illegible] or greater) and water resistance has required [illegible] stages such as autoclave treatment, pressing, or coating by UV or [illegible]B treatment as well as large facilities and equipment. This has presented problems with manufacturability or economy.

Thus, the easy manufacture of products that hardened items that have high strength and water resistance, and especially, products that are thin and have large dimensions has been extremely difficult.

The inventor has devised the present invention has solved the problems of conventional inorganic products described above by, in order to make the air bubble ratio and air bubble diameter in the hardened material as small as possible, (1) maintaining the fluidity of the slurry and holding the volume of mixed water [illegible] to a volume extremely close to the [illegible] water content or [illegible] water content by using an acryl water-dispersing organic polymer that has moisture-reducing and water-dispersing effects (2) generating ettringite fibers to further reduce water and filling the spaces in the hardened material with these crystals, and (3) by using a mixture of hydraulic cement and hydraulic gypsum to realize their mutually complementary effects. And has found that it demonstrates superior water resistance and strength.

That is to say, the inventor has provided the present invention that is a hydraulic inorganic composition that is characterized in that it comprises a) 10 - 90 parts by weight of a hydraulic cement, b) 10 - 90 parts by weight of a hydraulic

gypsum, c) 17 - 25 parts by weight of water (including the moisture contained in the acryl water-dispersing organic polymer of d)), d) 2 - 16 parts by weight of an acrylic, water-dispersing organic polymer that has a moisture-reducing effect (solid portion converted), and e) 0.5 - 2.0 parts by weight of a moisture-reducing agent.

The hydraulic cement according to the present invention may be a Portland cement, aluminate cement, white cement, blast furnace slag cement, silica fume cement, and so forth, commonly used in engineering construction, and may be used singly or in some combination thereof. The hydraulic gypsum may be a calcined gypsum (alpha form or beta form) or anhydrous gypsum and may be used singly or in some combination thereof. The ratio by weight of hydraulic cement to hydraulic gypsum is in the range 10 : 90 - 90 : 10, but when the hydraulic cement is less than 10 parts by weight or when the hydraulic gypsum is less than 10 parts by weight, the properties that are the objective of the present invention cannot be obtained, and especially, cracking, etc. has been observed when the hydraulic cement is greater than 90 parts by weight.

The water-dispersing organic polymer according to the present invention refers to a polymer in which minute particles

are dispersed homogeneously in water and which forms a so-called [illegible] latex or emulsion, and may be, broadly classified, a vinyl acetate, an acryl, a chlorine-containing vinyl polymer, a compound rubber, etc. However, when mixed with a hydraulic inorganic material, an acryl is preferred because it does not reduce the fluidity of the mixture and it produces a water-reducing effect, yet it still generates high strength, water resistance, etc., in the hardened material. In other words, copolymers of an acrylate ester and a methacrylate ester are indicated as the acryl water-dispersing organic polymer, but this includes copolymers that contain approximately one half or more of an acrylic monomer. Of these, a material that generates a water-reducing effect and maintains the fluidity of the slurry, that has a high film strength, and that is superior in water resistance, alkali resistance, [illegible] resistance, and polish is preferred, specifically methyl methacrylate-2-ethylhexylacrylate, styrene-butyl acrylate, etc. Here, to obtain the required water resistance and high strength, the amount of [illegible] water is reduced as much as possible to approach the theoretical moisture content, but this can be accomplished by mixing moisture-reducing agents with these acryl water-dispersing organic polymers that possess moisture reducing

properties. However, little improvement in water resistance and strength, etc., is observed when the amount of acryl water-dispersing organic polymer used is 2 parts by weight or less. In addition, volumes of 16 parts by weight or more are disadvantageous from the viewpoint of cost, and since no improvement in strength is observed, the volume of acryl water-dispersing organic polymer with moisture-reducing effect that is used is in the range 2 - 16 parts by weight, preferably 4 - 12 parts by weight (both converted to solids), with respect to 100 parts by weight of a mixture of hydraulic cement and hydraulic gypsum. In this way, since the dispersibility of the mixture of hydraulic cement and hydraulic gypsum is improved and the moisture-reducing effect and strength appearance in the hardened material are further improved, a moisture-reducing agent for general cement use is used. Specific examples are sodium lignin sulfonate, sodium salts of melamine sulfonate formaldehyde condensate, sodium salts of β -naphthalene sulfonate formaldehyde condensate, sodium salts of creosol sulfonate formaldehyde condensate, etc., but sodium salts of melamine sulfonate formaldehyde condensate are most preferred.

The amount to be added is in the range 0.5 - 2.0 parts by weight, preferable 0.5 - 1.0 parts by weight, with respect to 100 parts by weight of the mixture of hydraulic cement and hydraulic gypsum.

An amount of mixed water that is the theoretical volume of water or is extremely close to the theoretical volume of water is sufficient and is in the range 17 - 25 parts by weight, preferably 17 - 20 parts by weight, with respect to 100 parts by weight of the mixture of hydraulic cement and hydraulic gypsum, but this includes the water content of the acryl water-dispersing organic polymer, and according to the amount of acryl water-dispersing organic polymer used, the water content of this may be sufficient and the addition of water is unneeded, and even when needed, the amount of water added is up to a maximum of 15 parts by weight. Note that, even with 17 - 25 parts by weight of water, fluidity of the slurry is sufficiently maintained, foaming and defoaming is easy, poured shapes can be formed easily. The reason is that, with a water volume of less than 17 parts by weight, the amount of water required for hydrophilia with the hydraulic materials is insufficient, and with a volume of more than 25 parts by weight, the amount of water is excessive and sufficient physical characteristics cannot be obtained.

In the present invention, strengthening agents, fillers, etc.,

can be added to further improve the physical characteristics of the hardened material. Strengthening agents used may be inorganic materials such as glass fibers, slag fibers, rock wool, asbestos, etc., organic materials such as polypropylene, vinyl polychloride, polyester, polyamide, etc., fibrous strengtheners from woody fibers such as pulp, used paper, sawdust, flax, cotton, etc., or fine particle diameter powder strengtheners such as carbon black, aluminum hydroxide, calcium carbonate, magnesium carbonate, white carbon, titanium dioxide, etc. The volume of these strengtheners is in the range 0.5 - 10 parts by weight with respect to 100 parts by weight of the mixture of hydraulic cement and hydraulic gypsum. Additionally, fillers may be talc, mica, barite, [illegible] powder, etc. Further, suitable amounts of publicly known defoaming agents, hardening accelerating agents, hardening slowing agents, water-repelling agents, water-resisting agents, coloring agents, etc., may be added as needed. Moreover, the surfaces of hardened items formed from the water-dispersing inorganic composition according to the present invention may be treated with hard coating materials such as silicon or ceramic coating materials to form a membrane film that will further improve dirt resistance, abrasion resistance, damage resistance, chemical resistance, contaminant resistance, polish, water resistance, etc.

When manufacturing a hardened item from the water-dispersing inorganic composition according to the present invention, the fluidity of the slurry is very good, despite the low volume of water content, and foaming and defoaming can be conducted easily. As a result, items can be formed by pouring after excitation defoaming methods that add a defoaming agent and use a table vibrator or vacuum stirring foaming methods have been used. This slurry is self-leveling, so that the formation of flat items is especially easy. Hardened items removed from molds can be heated at 60 - 100°C for four hours or more following natural [illegible] in a humid environment. When an acryl water-dispersing organic polymer that cannot be formed at normal temperatures is used, heating to the range of minimum forming temperature to 100°C is needed.

The water-dispersing inorganic composition according to the present invention does not require large scale facilities and equipment and hardened items can be obtained very easily at low cost and can be made into thin shapes with especially large dimensions. Moreover, these hardened items have high strength, are excellent in water resistance, incombustibility, dirt resistance, vibration absorption, etc. Moreover, it is characterized in that yields are high due to almost no deformation or cracking during

manufacture and shape reproducibility is extremely good because swelling and shrinkage is extremely small. In addition, it has the effect that hardened items with extremely high polish can be obtained when molds with mirror surfaces are used.

Accordingly, the water-dispersing inorganic composition according to the present invention can be used widely as an engineering material such as tiles, blocks, paving stones, [illegible], interior and exterior [illegible] wall materials, flooring materials, ceiling materials, platform materials, interior materials, novelties, sound materials, vibration-absorbing materials ([illegible] materials), etc.

Next, the present invention will be further explained using embodiments. Note that for flex strength tests, specimens were formed with the dimensions 40 x 160 x 8 [illegible], and the test equipment used was a Shimazu Engineering Co., Ltd. Model JS500 autograph. Tests were conducted in accordance with JIS standards.

Embodiment 1

One part by weight (hereafter simply called "part") of a powdered water-reducing agent (a sodium salt of melamine sulfonate formaldehyde) was dissolved beforehand in 5 parts of water. To this, 20 parts of an ester acrylate copolymer emulsion (converted solids, 8 parts) were added to form an aqueous paste.

To this was added a mixture of 20 parts of α form calcined gypsum, 80 parts of Portland cement, and 3 parts of glass fibers (chopped strands). The resulting solution was agitated and stirred at 550 rpm for 5 minutes (during this period, a suitable volume of a silicon defoaming agent was dripped into the solution) to obtain a slurry with excellent fluidity. This slurry was defoamed on a table vibrator for 5 minutes and was then poured into a plastic mold with a mirror surface and was hardened. Following hardening and removal from the mold, the material was [illegible] at normal temperature, and was then heated for 4 hours at 70 - 75°C, and further, for 30 minutes at 90 - 95°C. This hardened item had a high polish, its flex strength was 306.5 kg/[illegible], and its absorbed water ratio (after submersion for 24 hours) was 0.51%.

Embodiment 2

A slurry produced in the same manner as Embodiment 1 was poured into a glass [illegible] with the dimensions 440 x 500 [illegible] to a depth of 5 [illegible] to obtain a hardened item. When the item was [illegible] and heated under the same conditions as Embodiment 1, there was almost no swelling or shrinkage and no deformation or cracking, so that a high strength, high polish product with large dimensions was obtained.

Embodiment 3

0.5 parts of a powdered water-reducing agent (a sodium salt of melamine sulfonate formaldehyde) was dissolved beforehand in 5 parts of water. To this, 20 parts of an ester acrylate copolymer emulsion (converted solids, 8 parts) were added to form an aqueous paste. To this was added a mixture of 60 parts of α form calcined gypsum, 40 parts of aluminate cement, 5 parts of carbon black, and 3 parts of glass fibers (chopped strands). The resulting solution was agitated and stirred at 550 rpm for 5 minutes (during this period, a suitable volume of a silicon defoaming agent was dripped into the solution) to obtain a slurry with excellent fluidity. After pouring, defoaming, [illegible], and heated in the same manner as Embodiment 1, the material flex strength was 268.2 kg/[illegible], and its absorbed water ratio (after submersion for 24 hours) was 0.55%.

Patent Applicant: Inoue, Hiroyuki

⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑪ 公開特許公報(A) 昭60-171260

⑫ Int.Cl.⁴ 識別記号 庁内整理番号 ⑬ 公開 昭和60年(1985)9月4日
C 04 B 28/00 7059-4G
//C 04 B 28/00 7059-4G
24:26 7059-4G 審査請求 未請求 発明の数 1 (全4頁)
22:00

⑭ 発明の名称 水硬性無機質組成物

⑮ 特 願 昭59-28234

⑯ 出 願 昭59(1984)2月16日

⑰ 発 明 者 井 上 博 之 大田市大田町大田ハの263

⑱ 出 願 人 井 上 博 之 大田市大田町大田ハの263

明 願 書

1. 発明の名称

水硬性無機質組成物

2. 特許請求の範囲

- a) 水硬性セメント 10～90重量部
 - b) 水硬性石膏 10～90重量部
 - c) 水 17～25重量部(但し、d)のアクリル系水分散性有機重合体中の水分量も含む)
 - d) 減水効果を有するアクリル系水分散性有機重合体 2～16重量部(但し、固形分換算)および
 - e) 減水剤 0.5～2.0重量部
- から成ることを特徴とする、水硬性無機質組成物。

3. 発明の詳細な説明

本発明は、変形、亀裂の発生がなく耐水性および高強度を発現し、大寸法で成形の硬化体をも簡単に成形し得る水硬性無機質組成物に関する。

従前より無機質製品としてはセメント、石膏、粘土質のもの、あるいは無機組成物に有機重合体または無機化合物を配合したもの等の既存製品があるが、セメント質のものは低破壊じん性、低曲げ強度、エフロレッセンスの発生、収縮亀裂の発生、強度発現が遅い等の観点があり、また石膏質のものは機械的強度が小さく耐水性に劣り、粘土質のものは機械的強度を大きくするためには高温焼成が必要であり、乾燥、焼成工程における変形、亀裂等の発生による歩留りの低下等の観点がある。そしてまた、セメント-石膏組成物に各種の水分散性有機重合体を配合した無機質製品は従前より多数開発されているが、その殆どは機械的強度、耐水性等において劣っており、かなりの強度(曲げ強度200kg/cm以上)および耐水性を発現するに到った成形物は、その製造においてオートクレーブ処理、プレス成形あるいはUV、EB処理によるコーティング等の煩雑な工程および大きな設備機器を要し、その生産性あるいは経済性において問題を強めている。

従って、高強度および耐水性を有する硬化体、なかんずく大寸法で薄形の製品を簡易に製造することは極めて困難であった。

本発明者は、硬化体中の気孔率、気孔径をできるだけ小さくするために、(1)減水剤および減水効果を有するアクリル系水分散性有機重合体を使用することにより、スラリーの流動性を保持し、混水量を理論水分量あるいは理論水分量に極く近似の量に抑えること、(2)エトリンガイトを生成させるに減水するとともに硬化体中の空隙をこの結晶で充填すること、(3)水硬性セメントと水硬性石膏の混合使用による互いの補完効果の発現により既存の無機質製品が有する上記の諸点を解消するとともに、優れた耐水性および強度を発現するとの知見により本発明に係る水硬性無機質組成物を得るに至った。

すなわち本発明は、(a)水硬性セメント10～90重量部、(b)水硬性石膏10～90重量部、(c)水17～25重量部(但し、(a)のアクリル系水分散性有機重合体中の水分量も含む)、(d)

減水効果を有するアクリル系水分散性有機重合体2～16重量部(但し、固形分換算)および(1)減水剤0.5～2.0重量部から成ることを特徴とする水硬性無機質組成物を提供することにある。

本発明における水硬性セメントとしては、通常工業的に製造されるポルトランドセメント、アルミナセメント、白色セメント、高炉セメント、シリカセメント等が挙げられるが、これらは単独または混合して用いることができる。また水硬性石膏としては、上記と同様に通常工業的に製造される半水石膏(α 型、 β 型)、無水石膏が使用されるが、これらも単独または混合して用いることができる。水硬性セメントと水硬性石膏の重量比は10:90～90:10であるが、水硬性セメントが10重量部以下あるいは水硬性石膏が10重量部以下であると、本発明の所期の目的である物性を得ることができず、特に水硬性セメントが90重量部以上になると亀裂等の発生が見られる。

本発明において水分散性有機重合体とは、その微細粒子が水の中に均一分散して、所謂ラッ

クスまたはエマルジョンと呼ばれる形態になっているものを意味し、大別すると酢酸ビニル系、アクリル系、塩素含有ビニルポリマー系、合成ゴム系等があるが、水硬性無機質材料と混合した時、混合物の流動性を低下させず、減水効果を生じ、しかも硬化体が高強度、耐水性等を発現するのはアクリル系のものが最良である。すなわち、アクリル系水分散性有機重合体とは、アクリル酸エステルとメタクリル酸エステルとの共重合体を指すが、ほぼ半量以上のアクリルモノマーが含有される共重合体も包含される。中でも、減水効果を発現するとともにスラリーの流動性を保持し、フィルム強度が大きく、耐水性、耐アルカリ性、耐蝕性、充沢性に優れた特性を有するものが好ましく、具体的にはメチルメタクリレート-2-エチルヘキシルアクリレート、ステレン-ブチルアクリレート等が挙げられる。そこで所期の耐水性および高強度等を得るには、混水量を可能な限り減少せしめ理論水分量に近づけることであるが、減水剤および減水効果を有するこれらのアクリル系水分散性

有機重合体を混合することにより可能となる。しかし、アクリル系水分散性有機重合体の使用量が2重量部以下であると耐水性および強度等の向上はあまり認められず、また16重量部以上ではコスト面において不利になり、且つ強度の一面の向上は認められないので、減水効果を有するアクリル系水分散性有機重合体の使用量は水硬性セメントと水硬性石膏の混合物100重量部に対して2～16重量部、好ましくは4～12重量部(但し、いずれも固形分換算)の範囲である。そして、水硬性セメントおよび水硬性石膏の分散性を良くし延いては減水効果および硬化体の強度発現を一層大きくするために、通常のセメント用減水剤が使用される。具体的にはリグニンスルホン酸ナトリウム、メラミンスルホン酸ホルムアルデヒド縮合物ナトリウム塩、 β -ナフタリンスルホン酸ホルムアルデヒド縮合物ナトリウム塩、クレゾールスルホン酸ホルムアルデヒド縮合物ナトリウム塩等が挙げられるが、メラミンスルホン酸ホルムアルデヒド縮合物ナトリウム塩が最も好ましく、その

添加量は水硬性セメントと水硬性石膏の混合物100重量部に対して0.5～2.0重量部、好ましくは0.5～1.0重量部である。

混水量は、理論水分量あるいは理論水分量に極く近似の量で充分であり、水硬性セメントと水硬性石膏の混合物100重量部に対して17～25重量部、好ましくは17～20重量部であるが、これはアクリル系水分散性有機重合体中の水分量をも含んでおり、アクリル系水分散性有機重合体の使用量によっては、これに含まれる水分量だけで充分で水の添加は不要であり、必要な場合でも水の添加量は最高15重量部までである。尚、混水量が17～25重量部でもスラリーの流動性は充分保持されており、脱泡、消泡も容易にでき、流込み成形も簡易にできる状態にある。因に、混水量が17重量部以下では水硬性材料の水和に必要な水分量に不足し、また25重量部以上では過剰水となり充分な物性を発現しない。

本発明において、硬化体の物性を更に向上させるために公知の補強材、充填材等を配合すること

ができる。補強材としては、ガラス繊維、スラグ繊維、ロックウール、石棉等の無機繊維やポリプロピレン、ポリ塩化ビニル、ポリエステル、ポリアミド等の有機繊維、あるいはバルブ、故紙、木粉、麻、綿等の木質系繊維から成る繊維質補強材、さらにカーボンブラック、水酸化アルミニウム、炭酸カルシウム、炭酸マグネシウム、ホワイトカーボン、二酸化チタン等の微粒子径粉末の補強材が使用できる。これら補強材の配合量は、水硬性セメントと水硬性石膏の混合物100重量部に対して0.5～10重量部である。また、充填材としては、タルク、マイカ、パーライト、陶石粉等が使用される。そしてまた、公知の消泡剤、硬化促進剤、硬化遅延剤、はっ水剤、耐水化剤、着色剤等を必要に応じて適宜添加することができる。更に、本発明に係る水硬性無機質組成物から得られた硬化体の表面にシリコン等のハードコート材あるいはセラミックコーティング材等を処理することにより被膜を形成し、耐候性、耐摩耗性、耐腐蝕性、耐薬品性、耐汚染性、光沢性、耐水性等

を一層向上させることもできる。

本発明に係る水硬性無機質組成物から硬化体を製造するに際しては、低混水量にもかかわらずスラリーの流動性は非常に良好であり脱泡、消泡が容易にできるために、消泡剤の添加およびタイゲルパイプレーター等を使用した加振消泡による方法、あるいは真空攪拌脱泡法等により脱泡した後、流込みによる成形が可能である。また、このスラリーはセルフレベルリング性を有するためにフラットな成形物の製造は殊に簡易に成し得る。そして脱型した硬化体は真空自然養生の後、60～100℃、4時間以上の加熱が適当であり、常温成膜性のないアクリル系水分散性有機重合体を使用する場合には、最低成膜温度以上～100℃の加熱が必要である。

本発明に係る水硬性無機質組成物は、大規模設備機器を要することなく極めて簡易かつ安価に硬化体を、なにかんづく大寸法で薄形の硬化体をも得ることができ、しかもその硬化体は高強度であり耐水性、不燃性、耐候性、吸水性等に優れ、また

その製造において変形、亀裂の発生が殆んどなく尙少留りで、膨脹収縮が極めて少なく超再現性が非常に良好であるという特徴を有する。そしてまた、鏡面を有する型を使用した場合には、極めて高光沢の硬化体を得る効果をも有する。

従って、本発明に係る水硬性無機質組成物は、タイル、ブロック、磁石、屋根材、内外装壁材、床材、天井材、置物台材、インテリア材、ノベルティ、音響材、振動吸収材（制振材）等の工業材料として広汎に利用できるものである。

次に実施例により本発明をさらに詳細に説明する。尚、曲げ強度試験は、試験片として40×160×8-のものを作成し、試験装置は（株）島津製作所製のオートグラフI8500型を使用しJISに則り実施した。

実施例1

水5重量部（以下、単に部と称す。）に粉末状の減水剤（ノラミンスルホン酸カルムアルデヒド縮合物ナトリウム塩）1部を予め溶解し、これにアクリル酸エステル系共重合体エマルジョン20

部（固形分換算8部）を混合した湯液水に、α型半水石膏20部、ポルトランドセメント80部、およびガラス繊維（チョップドストランド）3部の混合物を投入し、550RPMで5分間攪拌混合（この間に、シリコン系消泡剤を適宜滴下する。）して、流動性の良好なスラリーを調製する。このスラリーをテーブルバイブレーター上で5分間加振脱泡後、鏡面を有するプラスチック型に流込み硬化させる。硬化後脱型し常温下で真空養生した後、70～75℃で4時間、更に90～95℃で30分間加熱する。この硬化体は高光沢を有し、曲げ強度は306.6 $\frac{\text{kg}}{\text{cm}^2}$ 、吸水率（24時間浸漬）は0.51%であった。

実施例2

実施例1と同様にして調製したスラリーを440×500mmの寸法のガラス製型に流込み厚さ5mmの硬化体を得た。この硬化体を実施例1と全く同様に真空養生後、加熱したところ膨脹収縮が殆んどなく、変形、亀裂を全く生じない寸法で薄形の高強度、高光沢製品を得た。

実施例3

水5部に粉末状の滅水剤（メラミンスルホン酸ホルムアルデヒド縮合物ナトリウム塩）0.5部を予め溶解し、これにアクリル酸エステル系共重合体エマルジョン20部（固形分換算8部）を混合した湯液水に、α型半水石膏60部、アルミナセメント40部、カーボンブラック5部およびガラス繊維（チョップドストランド）3部の混合物を投入し、550RPMで5分間攪拌混合（この間に、シリコン系消泡剤を適宜滴下する。）して、流動性の良好なスラリーを調製する。以下、実施例1と全く同様に流込み、脱型、真空養生後、加熱したところ曲げ強度：268.2 $\frac{\text{kg}}{\text{cm}^2}$ 、吸水率（24時間浸漬）：0.56%の高光沢硬化体を得た。

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